MOLECULAR DYNAMICS STUDY OF THE
GLASS TRANSITION IN CONFINED WATER

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Abstract. A molecular dynamics simulation of SPC/E water confined in a Silica pore is presented. The pore has been constructed to reproduce the average properties of a pore of Vycor glass. Due to the confinement and to the presence of a strong hydrophilic surface, the dynamic behaviour of the liquid appears to be strongly dependent on the hydration level. The approach to the glass transition of confined water is investigated on lowering hydration and on supercooling in the framework of Mode Coupling Theories. At higher hydrations two quite distinct subsets of water molecules are detectable. Those belonging to the first layer close to the substrate suffer a severe slowing down, while the remaining ones display a scenario typical of supercooled liquids approaching the kinetic glass transition.

1. INTRODUCTION

The study of the modification of the properties of confined water with respect to the bulk is highly interesting since in many technological and biological applications water is confined in porous media. Several experimental studies and computer simulations give evidence that the perturbation of the substrate and the geometrical confinement change the properties at freezing [1, 2], the mobility [3, 4] and the dynamical behaviour of water [5, 6]. Particularly attracting is the study of confined water in the supercooled region. It is well known that below $235K$ the crystallization process driven by the homogeneous nucleation prevents the observation of a transition to a glass phase of water [7]. Experimentally forbidden regions of the phase diagram of bulk water could become accessible through the study of confined water. Molecular dynamics (MD) can be a suitable tool for exploring the approach of water to vitrification. In recent years MD simulation of Simple Point Charge/ Extended SPC/E [8] water model potential in the supercooled phase found a kinetic glass transition at a critical temperature T_C, as defined in the Mode Coupling Theory (MCT), which is $T_C \sim T_S$ [9], where T_S is the singular temperature of water [10], which is $T_S = 228K$ or, for SPC/E, 49 degrees below the temperature of maximum density. In many experimental studies [5] on confined or interfacial water a slowing down of the dynamics of the liquid with respect to the bulk water has been found with inelastic neutron scattering and NMR spectroscopy . It has been inferred from experiments that confining water could be equivalent to the supercooling of the bulk [11, 5]. Reduced self diffusion coefficient of water in contact with solid hydrophilic surfaces, when compared to bulk water are found in some of the computer simulation studies [3] but it is still difficult to find general trends in the dynamical properties of confined water and there are not any systematic studies in the supercooled region. Among the different systems studied experimentally water confined in porous Vycor glass is one of the most interesting with relevance to catalytic processes and enzymatic activity. Vycor is a porous silica glass with a quite well characterized structure of cylindrical pores and a quite sharp distribution of the pore sizes around the average value of $\sim 40 \pm 5\text{\AA}$. Several experiments on water-in-Vycor have been performed [5, 12]. We present here results obtained from MD simulations of the single particle dynamics of SPC/E water confined in a cylindrical silica cavity modeled to represent the average properties of Vycor pores [13]. The SPC/E potential used for water molecules models a single water molecule as a rigid set of interaction sites with an OH distance of 0.1 nm and a HOH angle equal to the tetrahedral angle 109.47^o. The Coulomb charges are placed on the atoms. Oxygens atoms additionally interact via a Lennard-Jones potential. SPC/E is particularly suitable for the study of dynamics in the supercooled region since it has been explicitly parametrized to reproduce not only the density but also the experimental value of the self diffusion constant at ambient conditions and moreover it is able to reproduce the temperature of maximum density of water. In our study we will focus on the dynamics of confined water at room temperature where both on lowering the hydration and on supercooling we observe a splitting of the time scale in the relaxation laws.

2. SLOW DYNAMICS OF WATER CONFINED IN VYCOR

In our simulation we build up a cubic cell of silica glass of $71\text{\AA}$ with a cylindrical cavity of $40\text{\AA}$ of diameter as described in detail in previous works [13]. The inner surface of the cylinder is then corrugated by removing all the silicon atoms bonded to less than four oxygens. The oxygens dangling bonds are then saturated with acidic hydrogens
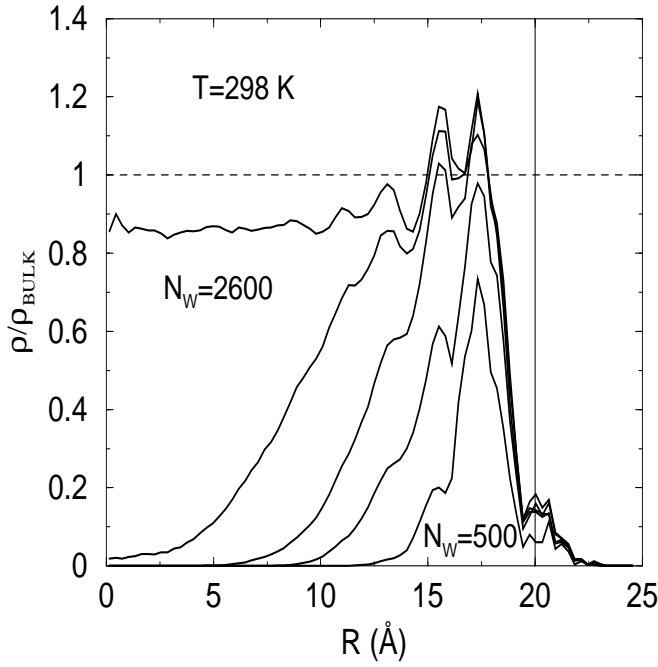
Figure 1. Radial density profiles normalized to the bulk for oxygen atoms at ambient temperature for the hydration levels investigated (see text). Curves on the top correspond to higher levels of hydration.
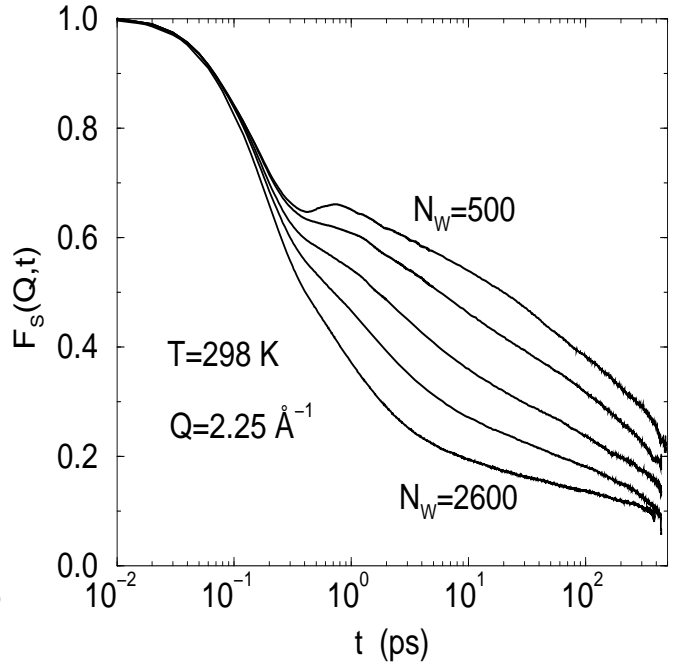
Figure 2. Self intermediate scattering function of oxygens for ambient temperature at the peak of the structure factor for the hydration levels investigated. Curves on the top correspond to lower levels of hydration.

in analogy with the experimental preparation of the sample of Vycor before hydration. Water molecules interact with the substrate atoms using an empirical potential model [13, 14]. The periodic boundary conditions are applied along the axis of the cylinder.

The molecular dynamics calculations have been performed for different numbers of SPC/E water molecules, introduced in the pore, corresponding to different levels of hydration: $N_W = 2600$ corresponding to 96% of hydration level of the pore, $N_W = 2000$ (74%), $N_W = 1500$ (56%), $N_W = 1000$ (37%) and $N_W = 500$ (19%). We will discuss here the results obtained for two temperatures: $T = 298\ K$ for all the hydrations and $T = 240\ K$ for $N_W = 1500$. A more detailed report will be published elsewhere [15]. As a first result we show in Fig.1 the density profiles along the pore radius. Already at lower hydrations the presence of a layer of water molecules wetting the substrate surface is observed. At nearly full hydration two layers of water with higher than bulk density are evident. There is a strong tendency of water molecules close to the surface to form hydrogen bonds (HB) with the atoms of the substrate [13].

In the MCT [16] description of a liquid approaching the glass transition the dynamic behaviour is mastered by the "cage effect". The molecule is trapped by the transient cage formed by its nearest neighbours. Signatures of the MCT behaviour can be found in the intermediate scattering function, ISF $F_S(Q, t)$, which will be shown below for our system. We expect to observe a diversification of the relaxation times resulting in a development of a shoulder in the relaxation laws. The long time tail of the ISF is predicted to have a stretched exponential behaviour when the system approaches the glass transition in the framework of MCT. In Fig.2 we present the ISF for the water oxygens at the oxygen-oxygen peak of the structure factor. The ISF are displayed at room temperature for the different hydrations. Upon decreasing hydration level the development of the shoulder in the relaxation laws is evident.

All the tails of the correlators of Fig.2 are highly non-exponential. None-the-less these ISF could not be fitted to the same formula used for bulk supercooled water [9],

$$F_S(Q, t) = [1 - A(Q)]\, e^{-(t/\tau_s)^2} + A(Q) e^{-(t/\tau_l)^\beta} \tag{1}$$

where $A(Q) = e^{-a^2 Q^2/3}$ is the Lamb-Mössbauer factor (the analogous of the Debye Waller Factor for the single particle) arising from the cage effect, τ_s and τ_l are, respectively, the short and the long relaxation times and β is the Kohlrausch exponent. Due to the strong hydrophilicity of the pore we observe a diversification of dynamic behaviour as we proceed from the pore surface to the center of the pore. The function $F_S(Q, t)$ is therefore splitted into the contribution coming from the two layers of water molecules closer to the pore surface (outer shells) and the contribution coming from all the remaining ones (inner shells) as displayed in Fig.1. The shell contribution is given only by the particles that move in the selected shell. We find that the inner shell contribution could be perfectly fit to eq.1, while the outer shells one decays to zero over a much longer timescale so that water molecules there behave already as a glass.
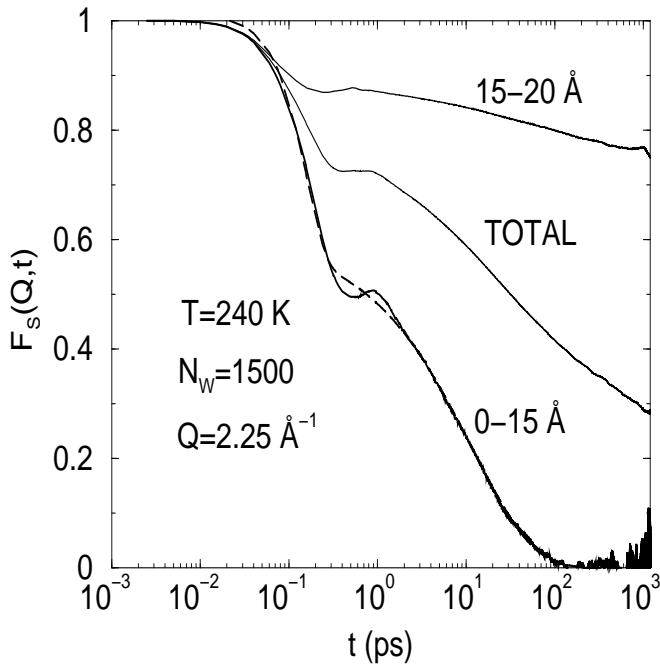
Figure 3. Shell analysis of the self intermediate scattering function (ISF) for oxygens at $T = 240\ K$ and $N_W = 1500$ (roughly half hydration). The curve on the top corresponds to the contribution to the ISF coming from the water molecules moving in the two layers closer to the substrate (outer shells), see Fig.1. The curve on the bottom (continuous line) represents the contribution of the remaining water molecules that move closer to the center of the pore (inner shells). The dashed line is the fit to eq.1. The central curve displays the total contribution.
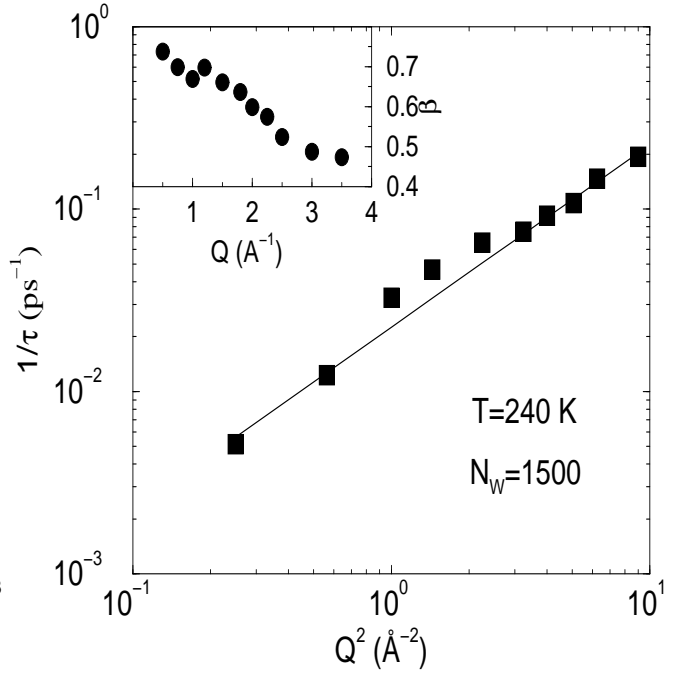
Figure 4. Values of τ_l vs. Q^2 (main picture) and β vs Q (inset) extracted from the fits of the intermediate scattering function to eq.1 (see text). The line with slope 1 (continuous line) in the main picture has been drown as a guideline for the eyes.

The double step relaxation observed for the lowest hydration deserves some comment. In fact for $N_W = 500$ the surface coverage is not complete and patches of water molecules are visible along the pore surface. The MCT is able to account also for the dynamics of clusters in a frozen environment [16] and this might be the reason of the development of the diversification of the relaxation law. From our analysis of ISF turns out that the behaviour of molecules belonging to the first hydration layers changes as a complete surface coverage is achieved.

In Fig.3 we show an example of the shell analysis for T=240 K and $N_W = 1500$. The top curve is the contribution to the total ISF coming from the molecules in the two shells closest to the substrate. The bottom curve is the contribution from the molecules in the remaining shells. The central one is the total ISF. The dashed line is the fit to eq.1. From the fit we obtain $\beta = 0.62$, $\tau_l = 11\ ps$ $\tau_s = 0.16\ ps$. The τ_l is similar to that of bulk water at the same temperature while the β is much lower. For the inner shells a bump around $0.7 ps$ is also observed that could possibly be related to the existence of the Boson Peak feature in the $S(q, \omega)$ [17]. This bump also appears in Fig.2 for the lowest hydration level investigated, namely 19%. In Fig.4 the τ_l and the β values extracted from the fits to eq.1 are plotted as a function of Q for T=240 K and $N_W = 1500$. The β value reaches a plateau value and the τ_l values show a Q^2 dependence. Both these behaviours are found in some glass former undergoing a kinetic glass transition and in particular the Q^2 behaviour has been observed for example in glycerol close to the glass transition [18]. However other behaviours of the relaxation times as a function of Q have been also found [19].

3. CONCLUDING REMARKS

We report some of the results achieved in the computer simulation of the dynamics of water molecules confined in a silica pore. The substrate is carefully modeled to reproduce the main features of the hydrophilic cavity of Vycor glass. In the water density profile we observe at high hydration levels a double layer structure which strongly influences the dynamics of the molecules.

An analogy between supercooled bulk water and confined water as a function of hydration level of the pore is possible in the sense that upon decreasing the hydration level a glassy behaviour appears already at ambient temperature. None-the-less the approach of confined liquid to the kinetic glass transition is rather different with respect to its bulk phase. In particular two quite distinct subsets of water molecules are detectable for confined water. The subset that is in contact with the surface is at higher density with respect to the bulk and is already a glass with low mobility even at ambient temperature. The inner subset displays, like a supercooled liquid, a two step relaxation

behaviour. The shape of the ISF long time tail, also called late part of the α-relaxation region, can be perfectly fitted to a stretched exponential function. The β and τ_l behaviours are consistent with the values extracted for other glass formers in literature.

More simulations on this system as function of temperature and hydration are in progress for a full MCT test and a complete comparison with the bulk. The relation between the two types of subsets and the so called *free* and *bound* water found in several experiments on confined water at freezing [1] is worthwhile to be explored in the future.

Acknowledgments

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